Many-body procedure for energy-dependent perturbation: Merging many-body perturbation theory with QED

Ingvar Lindgren*, Sten Salomonson†, and Daniel Hedendahl‡

Physics Department, Göteborg University, Göteborg, Sweden

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A formalism for energy-dependent many-body perturbation theory (MBPT), previously indicated in our recent review articles (Lindgren *et al.*, Phys.Rep. **389**,161(2004), Can.J.Phys. **83**,183(2005)), is developed in more detail. The formalism allows for a mixture of energy-dependent (retarded) and energy-independent (instantaneous) interactions and hence for a merger of QED and standard (relativistic) MBPT. This combination is particularly important for light elements, such as light heliumlike ions, where electron correlation is pronounced. It can also be quite significant in the medium-heavy mass range, as recently discussed by Fritzsche *et al.* (J.Phys. B**38**,S707(2005)), with the consequence that the effects might be significant also in analyzing the data of experiments with highly charged ions. A numerical procedure for treating the combined effect is described, and some preliminary numerical results are given for heliumlike ions. This represent the first numerical evaluation of effects beyond two-photon exchange involving a retarded interaction. It is found that for heliumlike neon the effect of one retarded photon (with Coulomb interactions of all orders) represents about 99% of the non-radiative effects beyond energy-independent MBPT.

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I. INTRODUCTION

What is commonly known as Many-Body Perturbation Theory (MBPT) is a class of perturbative schemes for bound atomic, molecular or nuclear states with a time- or energy-independent perturbation, based upon the Rayleigh-Schrödinger perturbative scheme, such as the Brueckner-Goldstone linked-diagram expansion or variants thereof [1]. Also certain iterative or "all-order" approaches, like the Coupled-Cluster Approach (CCA) or "Exponential Ansatz", can be referred to this category, although they are not strictly perturbative in nature. All these approaches can in principle treat the electron correlation to arbitrary order. In addition, they have—as distinct from procedures based upon the Brillouin-Wigner (BW) perturbation expansion—the important property of being *size extensive* in the sense that the energy scales linearly with the size of the system. Furthermore, by using an extended or multi-reference model space such schemes can also successfully handle the *quasidegenerate* problem with closely spaced energy levels that are strongly mixed by the perturbation.

For time- or energy dependent perturbations, like those of quantum-electrodynamics (QED), the situation is quite different and much less developed. There is presently no numerical scheme available that can treat energy-dependent perturbations together with electron correlation to arbitrary order, and also the treatment of quasidegeneracy forms a serious problem in connection with such interactions. In the numerical methods presently available for QED calculations the electron-electron interaction is treated by the exchange of fully covariant photons, which is quite a tedious—and usually unnecessarily tedious—process to handle the electron correlation. At most two-photon exchange can be treated in this way with computers available today, which is insufficient for light and medium-heavy elements, where the electron correlation is quite important.

A major problem in extending the energy-dependent perturbation theory to include electron correlation is that most methods have a structure that is quite different from that of energy-independent perturbation theory, which makes it difficult to utilize the well-developed methods of the latter. Of the available methods only the *Covariant Evolution Operator* (CEO) method that we recently developed, has a structure that is akin to standard energy-independent MBPT [2, 3, 4]. This opens the possibility of combining the two approaches as proposed in our recent review articles [4, 5] and further developed in the present work. In that scheme the CEO method is combined with all-order MBPT methods of coupled-cluster type, so that the exchange of covariant photons can be mixed with an arbitrary number of instantaneous Coulomb interactions. In this way electron correlation can for the first time be treated to arbitrary order together with energy-dependent interactions of QED type.

* e-mail address: ingvar.lindgren@fy.chalmers.se

† e-mail address: f3asos@fy.chalmers.se

‡ e-mail address: dahe@fy.chalmers.se

The CEO method was originally developed in order to be able to treat the quasidegeneracy problem in QED calculations. The standard procedure for bound-state QED is the S-matrix formulation [6], which has been successfully applied particularly to highly charged ions. For lighter elements—in addition to the electron-correlation problem— also the quasidegeneracy problem might be quite pronounced, and the S-matrix formulation fails. One illustrative example is the fine structure of heliumlike ions, where in the relativistic formulation for instance the lowest triplet state $^3P_1$ is a mixture of the basis states $1s2p_{1/2}$ and $1s2p_{3/2}$, which are very closely spaced in energy and strongly mixed for light elements. In order to be able to use the procedure of standard MBPT, where quasidegenerate states are included in an extended model space, off-diagonal elements of the effective Hamiltonian have to be evaluated, which is not possible in the standard S-matrix formulation, due to the energy conservation of the scattering process [7]. In the CEO method, based upon the evolution operator for *finite* time [4], the extended-model-space technique can be used, and a few years ago we applied this to evaluate QED contributions to the fine structure for heliumlike ions, including the quasidegenerate $^3P_1$ state, down to $Z = 9$ [3]. The same problem has very recently been treated by Shabaev *et al.* down to $Z = 12$, using the *two-times Green's function technique* [8, 9]. Furthermore, the presently available methods for numerical QED calculations suffer from the shortcoming that they are not applicable to the lightest elements—below Z=10, say—due to convergence problems. The extension of the CEO method to include electron correlation to arbitrary order, presented here, is expected to remedy this problem.

The most accurate calculations on light heliumlike ions have been performed by the analytical or "unified" method of Drake and related techniques [10, 11, 12, 13, 14]. This is based upon expansion in powers of the fine-structure constant α of the Bethe-Salpeter equation and the Brillouin-Wigner (BW) perturbation series [15, 16]. It leads to extremely high accuracy for the lightest elements, but there is still a significant discrepancy between theory and experiment for the lowest triplet state of neutral helium. Being based upon the BW perturbation expansion, the procedure is *not* size-extensive and less suitable for larger systems.

In addition to the light heliumlike ions and other light systems, the combination of QED and many-body effects can be of importance also for heavier systems, as recently discussed by Fritzsche *et al.* [17]. They have analyzed this problem particularly with regard to possible heavy-ion experiments of the type that can be performed at the big storage rings, like that at GSI in Darmstadt. They then conclude that the accurate treatment of the interplay between QED and many-body effects constitutes one of the most challenging problems in connection with highly-charged-ion experiments.

The present paper will be organized as follows. In the next section we briefly review the standard perturbation theory for time-independent and time-dependent perturbations, and next we summarize the properties of our recently introduced covariant evolution-operator method. The following main section deals with the derivation of Bloch equations for combined retarded and instantaneous interactions, which constitute our working equations for treating this problem. Finally, we describe briefly our numerical procedure and give some preliminary numerical results, including the first numerical result of effects beyond two-photon exchange with a retarded interaction. The numerical procedure together with more complete numerical results will be published separately [18].

II.   STANDARD MANY-BODY PERTURBATION THEORY

A.   Time-independent perturbation theory

In the multi-reference form of MBPT we consider a number of *target states* that are eigenstates of the Hamiltonian of the system

$$H \left| \Psi^\alpha \right\rangle = E^\alpha \left| \Psi^\alpha \right\rangle; \qquad (\alpha = 1, 2, \cdots d). \tag{1}$$

The Hamiltonian is partitioned into a model Hamiltonian, H_0, and a time-independent perturbation, H',

$$H = H_0 + H'. \tag{2}$$

For an N-electron system the model Hamiltonian is assumed to be composed of single-electron Schrödinger or Dirac Hamiltonians

$$H_0 = \sum_i^N h_0(i). \tag{3}$$

For each target state there is a model state, confined to a subspace, the *model space*, with the projection operator P. In the intermediate normalization we use here the model states are the projection of the corresponding target states

on the model space

$$|\Psi_0^\alpha\rangle = P|\Psi^\alpha\rangle. \tag{4}$$

A wave operator can be defined for the inverse transformation

$$|\Psi^\alpha\rangle = \Omega\,|\Psi_0^\alpha\rangle\,; \qquad (\alpha = 1, 2, \cdots d). \tag{5}$$

An *effective Hamiltonian* can be defined, $H_{\text{eff}} = PH\Omega P$, that operates in the model space and for which the eigenvectors are the model states and the eigenvalues the corresponding exact energies

$$H_{\text{eff}}\,|\Psi_0^\alpha\rangle = E^\alpha\,|\Psi_0^\alpha\rangle. \tag{6}$$

The corresponding *effective interaction* is defined

$$V_{\text{eff}} = H_{\text{eff}} - PH_0P = PH'\Omega P. \tag{7}$$

The wave operator satisfies the generalized Bloch equation [19, 20, 21]

$$\boxed{\big[\Omega, H_0\big]P = \big(H'\Omega - \Omega\,V_{\text{eff}}\big)P} \tag{8}$$

This leads to the Rayleigh-Schrödinger perturbative expansion for a general multi-reference (quasidegenerate) model space, and it can also be used to generate the corresponding linked-diagram expansion of Brueckner-Goldstone type

$$\big[\Omega, H_0\big]P = \big(H'\Omega - \Omega\,V_{\text{eff}}\big)_{\text{linked}}P. \tag{9}$$

Here, only so-called linked terms or diagrams survive on the right-hand side. Using the exponential Ansatz

$$\Omega = \{\mathrm{e}^S\}, \tag{10}$$

where the curly brackets represent normal-ordering, leads to the Coupled-Cluster expansion for the same model space [22]

$$\big[S, H_0\big]P = \big(H'\Omega - \Omega\,V_{\text{eff}}\big)_{\text{conn}}P. \tag{11}$$

Here, all terms on the right-hand side are "connected". (For the distinction between "linked" and "connected", see, for instance, ref. [1].

B.   Time-dependent perturbation theory

In this paper we shall only be concerned with *stationary states*, but we need for our purpose to use the formalism for time-dependent perturbation, which we shall briefly review.

The time-dependent state vector satisfies the time-dependent Schrödinger equation (using relativistic units $\hbar = c = m = \epsilon_0 = 1$)

$$\mathrm{i}\frac{\partial}{\partial t}\,|\chi(t)\rangle = H(t)\,|\chi(t)\rangle, \tag{12}$$

where

$$H(t) = H_0 + H'(t). \tag{13}$$

H_0 is the time-independent model Hamiltonian and $H'(t)$ is a perturbation that might be time-dependent. In the *interaction picture* (IP), where an operator is related to that in the *Schrödinger picture* (SP) by

$$O_{\text{I}}(t) = \mathrm{e}^{\mathrm{i}H_0t}O_{\text{S}}\,\mathrm{e}^{-\mathrm{i}H_0t} \tag{14}$$

the Schrödinger equation becomes

$$\mathrm{i}\frac{\partial}{\partial t}\,|\chi_{\text{I}}(t)\rangle = H'_{\text{I}}(t)\,|\chi_{\text{I}}(t)\rangle. \tag{15}$$

The *time-evolution operator* is defined by

$$|\chi_{\text{I}}(t)\rangle = U_{\text{I}}(t, t_0)\,|\chi_{\text{I}}(t_0)\rangle \tag{16}$$

and satisfies the equation

$$\mathrm{i}\frac{\partial}{\partial t}\,U_\mathrm{I}(t,t_0) = H'_\mathrm{I}(t)\,U_\mathrm{I}(t,t_0) \tag{17}$$

with the solution [23]

$$U_\mathrm{I}(t,t_0) = 1 + \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_{t_0}^{t} \mathrm{d}^4 x_n \cdots \int_{t_0}^{t} \mathrm{d}^4 x_1\, T_\mathrm{D}\big[\mathcal{H}'_\mathrm{I}(x_n)\mathcal{H}'_\mathrm{I}(x_{n-1})\cdots\mathcal{H}'_\mathrm{I}(x_1)\big]. \tag{18}$$

Here, T_D is the Dyson time-ordering operator, and $\mathcal{H}'_\mathrm{I}(x)$ is the perturbation *density*, defined by

$$H'_\mathrm{I}(t) = \int \mathrm{d}^3\boldsymbol{x}\,\mathcal{H}'_\mathrm{I}(t,\boldsymbol{x}). \tag{19}$$

An *adiabatic damping* is added to the perturbation

$$H'_\mathrm{I}(t) \to H'_{\mathrm{I}\gamma} = H'_\mathrm{I}\,\mathrm{e}^{-\gamma|t|}\,; \qquad U_\mathrm{I}(t,t_0) \to U_\gamma(t,t_0), \tag{20}$$

where γ is a small, positive number. This implies that as $t \to \pm\infty$ the eigenfunctions of H tend to eigenfunctions of H_0.

For stationary states we assume that the perturbation H' is time-independent in the Schrödinger picture—apart from the adiabatic-damping factor. Then according to the Gell-Mann–Low (GML) theorem [24] the wave function at time $t = 0$ is for a single-reference model space given by

$$|\Psi\rangle = |\chi(0)\rangle = \lim_{\gamma\to 0} \frac{U_\gamma(0,-\infty)\big|\Psi_0\big\rangle}{\langle\Psi_0|U_\gamma(0,-\infty)|\Psi_0\rangle}, \tag{21}$$

where $|\Psi_0\rangle$ is the time-independent model state. This can be generalized to a general multi-reference model space [4, Eq. 110]

$$|\Psi^\alpha\rangle = \lim_{\gamma\to 0} \frac{N^\alpha U_\gamma(0,-\infty)|\Phi^\alpha\rangle}{\langle\Phi^\alpha|U_\gamma(0,-\infty)|\Phi^\alpha\rangle}\,; \qquad (\alpha = 1, 2, \cdots d), \tag{22}$$

where N^α is a normalization factor and the vector $|\Phi^\alpha\rangle$ is defined

$$|\Phi^\alpha\rangle = \lim_{\gamma\to 0}\lim_{t\to-\infty} |\chi^\alpha(t)\rangle. \tag{23}$$

Then the wave function at time $t = 0$ satisfies the time-independent Schrödinger-like equation

$$\boxed{\big(H_0 + H'\big)\Psi^\alpha = E^\alpha\Psi^\alpha} \tag{24}$$

where H' is the time-independent perturbation in the Schrödinger picture.

The evolution operator normally contains singularities or quasi-singularities as $\gamma \to 0$, when an intermediate state is degenerate or closely degenerate with the initial state. In the GML formulas these (quasi-)singularities are eliminated by the denominator so that the ratio is always regular, which is one formulation of the linked-diagram theorem [25].

III.   COVARIANT EVOLUTION-OPERATOR APPROACH

(The reader is referred to refs [4, 5] for more details concerning the basic covariant evolution-operator formalism.)

A.   Interaction with the electro-magnetic field

We consider now the interaction between electrons and the quantized electro-magnetic field represented by the perturbation density [26]

$$\mathcal{H}'(x) = -e\hat{\psi}^\dagger \alpha^\mu A_\mu \hat{\psi}_\mathrm{H} \tag{25}$$

Here, $\hat{\psi}_{\mathrm{I}}$, $\hat{\psi}_{\mathrm{I}}^{\dagger}$ are the electron field operators, α^{μ} the Dirac alpha operators and A_{μ} is the radiation field

$$A_{\mu} \propto \varepsilon_{\mu}^{r} \left(a_{r}^{\dagger}(\boldsymbol{k}) \, e^{i\kappa x} + a_{r}(\boldsymbol{k}) \, e^{-i\kappa x} \right), \tag{26}$$

applying standard summation convention. $a_{r}^{\dagger}(\boldsymbol{k})$, $a_{r}(\boldsymbol{k})$ are the photon creation/absorption operators, $\boldsymbol{k}$ is the wave vector, κ is the four-vector momentum $\kappa = (\omega, -\boldsymbol{k})$ $(k = |\boldsymbol{k}|)$, and ε_{r}^{μ} represent the polarization vectors. The Hamiltonian of the radiation field is represented by

$$H_{\mathrm{rad}} = \omega \, a_{r}^{\dagger}(\boldsymbol{k}) a_{r}(\boldsymbol{k}) = k \, a_{r}^{\dagger}(\boldsymbol{k}) a_{r}(\boldsymbol{k}). \tag{27}$$
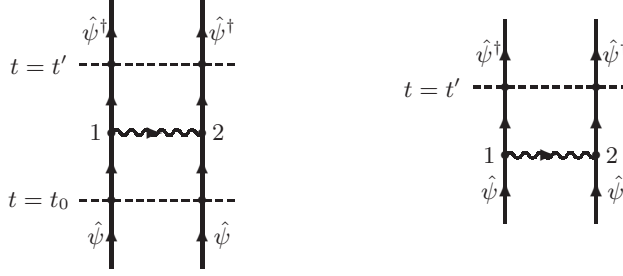

FIG. 1: Graphical representation of the covariant-evolution operator for single-photon exchange in the form (30) (left) and in the form (31) with $t_0 \to -\infty$.

With the interaction density (25) the evolution operator (18) for single-photon exchange becomes

$$U^{(2)}(t', t_0) = -\frac{1}{2} \iint_{-t_0}^{t'} \mathrm{d}^4 x_1 \mathrm{d}^4 x_2 \, \hat{\psi}_{\mathrm{I}+}^{\dagger}(x_1) \hat{\psi}_{\mathrm{I}+}^{\dagger}(x_2) \, \mathrm{i}I(x_1, x_2) \, \hat{\psi}_{\mathrm{I}+}(x_2) \hat{\psi}_{\mathrm{I}+}(x_1), \tag{28}$$

integrated over all space coordinates and time coordinates as indicated. $\hat{\psi}_{\mathrm{I}+}$, $\hat{\psi}_{\mathrm{I}+}^{\dagger}$ are the positive-energy part of the electron-field operators, and the interaction kernel

$$\mathrm{i}I(x_1, x_2) = (-e\alpha^{\mu} \overbrace{A_{\mu}})_1 (-e\alpha^{\nu} A_{\nu})_2 = e^2 \alpha_1^{\mu} \alpha_2^{\nu} \, \mathrm{i}D_{F\mu\nu}(x_1 - x_2) \tag{29}$$

is given by the product of two perturbations (25) with contraction of the radiation-field operators (indicated by the hook). $D_{\mathrm{F}\mu\nu}(x_1 - x_2)$ is the Feynman *photon propagator*.

The evolution operator above is *non-covariant* but can be made *covariant* by inserting zeroth-order Green's functions on the in- and outgoing states [3, 4]

$$\begin{aligned} U_{\mathrm{Cov}}^{(2)}(t', t_0) &= -\frac{1}{2} \iint \mathrm{d}^3 \boldsymbol{x}_1' \mathrm{d}^3 \boldsymbol{x}_2' \, \hat{\psi}_{\mathrm{I}}^{\dagger}(x_1') \hat{\psi}_{\mathrm{I}}^{\dagger}(x_2') \iint \mathrm{d}^4 x_1 \mathrm{d}^4 x_2 \, G_0(x_1', x_2'; x_1, x_2) \\ &\times \iint \mathrm{d}^3 \boldsymbol{x}_{10} \mathrm{d}^3 \boldsymbol{x}_{20} \, \mathrm{i}I(x_1, x_2) \, G_0(x_1, x_2; x_{10}, x_{20}) \, \hat{\psi}_{\mathrm{I}}(x_{20}) \hat{\psi}_{\mathrm{I}}(x_{10}). \end{aligned} \tag{30}$$

Here, the time integrations over t_1 and t_2 are performed over *all times*, and positive- as well as negative-energy states are allowed as incoming and outgoing states. The initial and final times are the same for the two electrons, i.e.,

$$t_{10} = t_{20} = t_0 \quad \text{and} \quad t_1' = t_2' = t'.$$

We shall in the following assume that the initial time is $t_0 = -\infty$, and then due to the adiabatic damping (20) we can leave out the rightmost Green's function [4]

$$U_{\mathrm{Cov}}^{(2)}(t', -\infty) = \frac{1}{2} \hat{\psi}_{\mathrm{I}}^{\dagger}(x_1') \hat{\psi}_{\mathrm{I}}^{\dagger}(x_2') \, G_0(x_1', x_2'; x_1, x_2) \, \mathrm{i}I(x_1, x_2) \, \hat{\psi}_{\mathrm{I}}(x_2) \hat{\psi}_{\mathrm{I}}(x_1). \tag{31}$$

Here, we have left out the integrations, and in the following we shall also leave out the subscript $_{\mathrm{Cov}}$ as well as the initial time.

B. Wave operator and effective interaction

The evolution operator is generally singular and can be expressed [4]

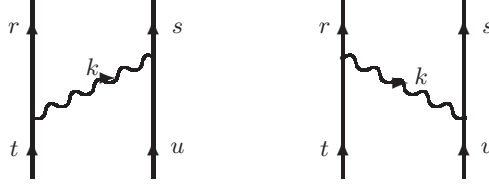$$U(t)P = P + \widetilde{U}(t)P \cdot PU(0)P \tag{32}$$

FIG. 2: Graphical representation of single-photon potential (41).

where $\widetilde{U}(t)$ is always regular and known as the *reduced evolution operator*—all singularities are collected in the last factor $PU(0)P$. The heavy dot indicates here that the two factors evolve in time independently from different model-space states. For the time $t = 0$ this becomes

$$U(0)P = \left[1 + Q\widetilde{U}(0)\right]P \cdot PU(0)P, \tag{33}$$

where Q is the projection operator for the "complementary space" (outside the model space).

Inserting the expression (33) into the GML formula (22), yields

$$|\Psi^\alpha\rangle = \left[1 + Q\widetilde{U}(0)\right]P \lim_{\gamma \to 0} \frac{N^\alpha U_\gamma(0, -\infty)|\Phi^\alpha\rangle}{\langle \Phi^\alpha|U_\gamma(0, -\infty)|\Phi^\alpha\rangle} = \left[1 + Q\widetilde{U}(0)\right]P|\Psi^\alpha\rangle. \tag{34}$$

But $P|\Psi^\alpha\rangle = \Psi_0^\alpha$ is the model state (4), and hence the expression in the square brackets represents the wave operator (5)

$$\boxed{\Omega = 1 + Q\widetilde{U}(0)} \tag{35}$$

The Q operator is for a two-electron system given by

$$Q = 1 - P = |rs\rangle\langle rs|, \tag{36}$$

where the ket vectors $|rs\rangle$ represent straight (non-antisymmetrized) products of single particle states, summed over all states outside the model space. The single-particle states are generated by the single-particle Hamiltonians (3)

$$h_0|i\rangle = \varepsilon_i|i\rangle, \tag{37}$$

which also include the nuclear field (Furry picture). In the two-electron system we shall study here, the occupied electron states are treated as open-shell or valence states, which implies that there are no core or hole states—apart from the negative-energy states.

Performing the integrations for the single-photon exchange (31), yields [3, 4]

$$\langle rs|U^{(2)}(t)|ab\rangle = \langle rs|e^{-it(E_{ab}-\varepsilon_r-\varepsilon_s)}\Gamma_Q(E_{ab})\mathcal{V}_1(E_{ab})|ab\rangle; \qquad E_{ab} = \varepsilon_a + \varepsilon_b \tag{38}$$

or, generally, operating on a model-space state of energy $\mathcal{E}$,

$$U^{(2)}(t)P = e^{-it(\mathcal{E}-H_0)}\Gamma_Q(\mathcal{E})\mathcal{V}_1(\mathcal{E})P. \tag{39}$$

Here,

$$\Gamma_Q(\mathcal{E}) = \frac{Q}{\mathcal{E} - H_0} \tag{40}$$

is the *resolvent*, and

$$\langle rs|\mathcal{V}_1(\mathcal{E})|tu\rangle = \left\langle rs\right| \int dk\, f(\boldsymbol{x}_1, \boldsymbol{x}_2, k)\left[\frac{1}{\mathcal{E} - \varepsilon_r - \varepsilon_u - (k - i\gamma)_r} + \frac{1}{\mathcal{E} - \varepsilon_s - \varepsilon_t - (k - i\gamma)_s}\right]\left|tu\right\rangle \tag{41}$$

is the matrix element of the potential, considering both time orderings (see Fig. 2). The subscript $_r$ represents the sign of ε_r. Using the evolution operator (39) and the relation (35) (with $\widetilde{U}^{(2)} = U^{(2)}$), this gives the wave operator for single-photon exchange

$$\Omega^{(1)}P = \Gamma_Q(\mathcal{E})\mathcal{V}_1(\mathcal{E})P \tag{42}$$

The effective interaction (7) can generally be expressed [4]

$$\boxed{V_{\text{eff}} = P\left[\mathrm{i}\frac{\partial}{\partial t}\widetilde{U}(t)\right]_{t=0}P}$$

(43)

The reduced evolution operator has the same time dependence in all orders as in first order (39), which implies that the time derivation eliminates the resolvent. In first order this yields

$$V_{\text{eff}}^{(1)}(\mathcal{E}) = P\mathcal{V}_1(\mathcal{E})\,P.$$

(44)

The function $f(\boldsymbol{x}_1, \boldsymbol{x}_2, k)$ in the potential (41) depends on the gauge used and is in the Feynman gauge given by

$$f_{\text{F}}(\boldsymbol{x}_1, \boldsymbol{x}_2, k) = -\frac{e^2}{4\pi^2}\,(1 - \boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2)\,\frac{\sin(kr_{12})}{r_{12}},$$

where r_{12} is the interelectronic distance.

In the Coulomb gauge, which is natural to use in many-body calculations, the potential can be separated into an *instantaneous* and a *retarded* part,

$$V(\mathcal{E}) = V_{\text{I}} + V_{\text{Ret}}(\mathcal{E}),$$

(45)

where only the latter is energy dependent. The instantaneous part is the Coulomb interaction

$$V_{\text{I}} = V_{12} = \frac{e^2}{4\pi r_{12}},$$

(46)

and the retarded part is given by the expression (41) with

$$f_{\text{C}}(\boldsymbol{x}_1, \boldsymbol{x}_2, k) = \frac{e^2}{4\pi^2}\left[-\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2\frac{\sin(kr_{12})}{r_{12}} + (\boldsymbol{\alpha}_1 \cdot \boldsymbol{\nabla}_1)(\boldsymbol{\alpha}_2 \cdot \boldsymbol{\nabla}_2)\frac{\sin(kr_{12})}{k^2\,r_{12}}\right],$$

(47)

where the nabla operators do not operate beyond the square bracket. Here, the first term represent the *Gaunt* part and the second term the *scalar-retardation* part, which together form the *Breit interaction*. In the following we shall assume that the Coulomb gauge is used.

The relations given here, particularly the framed equations (35) and (43), demonstrate the close analogy between the covariant evolution-operator approach and standard MBPT, which opens up the possibility for a merger of the two procedures.

IV. BLOCH EQUATION FOR INSTANTANEOUS AND RETARDED INTERACTIONS

A. Retarded interactions

From the definition (32), the following relation can be derived, using standard algebra [5],

$$\widetilde{U}(t)P = \bar{U}(t)P + \widetilde{U}(t)\left(P\bar{U}P - \cdot P\bar{U}P\right),$$

(48)

where

$$\bar{U}(t)P = \widetilde{U}(t)P - M(t)$$

(49)

is the evolution operator without intermediate model-space states and M is the *model-space contribution* (MSC). The $\bar{U}$ operator in Eq. (48) has the time argument $t = 0$.

As mentioned, in the product $\widetilde{U}(t)P\bar{U}(0)P$ the time-dependent part $\widetilde{U}(t)$ evolves from the energy of the state to the far right ($\mathcal{E}$), while in the dot product $\widetilde{U}(t) \cdot P\bar{U}(0)P$ the operator $\widetilde{U}(t)$ evolves from the energy of the intermediate state ($\mathcal{E}'$). Therefore, the second term, which represents the MSC part, becomes

$$M = (\widetilde{U}(\mathcal{E}) - \widetilde{U}(\mathcal{E}'))\,P\bar{U}P$$

(50)

This can be expressed

$$P\bar{U}P = \frac{\bar{V}_{\text{eff}}}{\mathcal{E} - \mathcal{E}'},$$

where $\bar{V}_{\text{eff}}$ is the analogue of the effective interaction (43) without MSC

$$\bar{V}_{\text{eff}} = P\left[i\frac{\partial}{\partial t}\bar{U}(t)\right]_{t=0} P. \tag{51}$$

This yields

$$M = \frac{\widetilde{U}(\mathcal{E}) - \widetilde{U}(\mathcal{E}')}{\mathcal{E} - \mathcal{E}'} \, \bar{V}_{\text{eff}} = \frac{\delta\widetilde{U}}{\delta\mathcal{E}} \, \bar{V}_{\text{eff}}, \tag{52}$$

using the difference ratio defined in Appendix B. This yields

$$\widetilde{U}(t)P = \bar{U}(t)P + \frac{\delta\bar{U}}{\delta\mathcal{E}} \, \bar{V}_{\text{eff}}. \tag{53}$$

With the wave-operator relation (35) we then have

$$\Omega P = \bar{\Omega}P + \frac{\delta\Omega}{\delta\mathcal{E}} \, \bar{V}_{\text{eff}}, \tag{54}$$

where the last term represents the MSC (including "folded" diagram) and $\bar{\Omega}$ is the wave operator without MSC.

The relation (48) leads to the expansion

$$\widetilde{U}(t)P = \bar{U}(t)P + \bar{U}(t)\left(P\bar{U}P - \cdot P\bar{U}P\right) + \bar{U}(t)\left(P\bar{U}P - \cdot P\bar{U}P\right)\left(P\bar{U}P - \cdot P\bar{U}P\right) + \cdots \tag{55}$$

The exchange of a single photon corresponds to the second-order evolution operator and leads to the result given above (42). The two-photon exchange corresponds to the next even order of the evolution operator

$$\widetilde{U}^{(4)}(t)P = \bar{U}^{(4)}(t)P + \bar{U}^{(2)}(t)\left(P\bar{U}^{(2)}P - \cdot P\bar{U}^{(2)}P\right). \tag{56}$$

Since there is no MSC in lowest order, we have $U^{(2)} = \bar{U}^{(2)} = \widetilde{U}^{(2)}$, and the corresponding wave operator becomes

$$\Omega^{(2)}P = Q\widetilde{U}^{(4)}(0)P = \bar{\Omega}^{(2)}P + \frac{\delta\Omega^{(1)}}{\delta\mathcal{E}} \, V_{\text{eff}}^{(1)}, \tag{57}$$

where $\bar{\Omega}^{(2)}P = \Gamma_Q \mathcal{V}_1 \Gamma_Q \mathcal{V}_1 P$. In the case of degeneracy this goes over into

$$\Omega^{(2)}P = \bar{\Omega}^{(2)}P + \frac{\partial\Omega^{(1)}}{\partial\mathcal{E}} \, V_{\text{eff}}^{(1)}. \tag{58}$$

In third order we have [5, App. D]

$$\Omega^{(3)}P = \bar{\Omega}^{(3)}P + \frac{\delta\Omega^{(2)}}{\delta\mathcal{E}} \, V_{\text{eff}}^{(1)} + \frac{\delta\Omega^{(1)}}{\delta\mathcal{E}} \, \bar{V}_{\text{eff}}^{(2)}, \tag{59}$$

which leads to

$$\Omega^{(3)}P = \bar{\Omega}^{(3)}P + \frac{\delta\Omega^{(1)}}{\delta\mathcal{E}} \, V_{\text{eff}}^{(2)} + \frac{\delta\bar{\Omega}^{(2)}}{\delta\mathcal{E}} \, V_{\text{eff}}^{(1)} + \frac{\delta^2\Omega^{(1)}}{\delta\mathcal{E}^2} \, \left(V_{\text{eff}}^{(1)}\right)^2, \tag{60}$$

where the second-order difference ratio is defined in Appendix B. The last term is associated with double model-space contributions ("double fold"). This leads to conjecture for the all-order expansion (c.f. [5, Eq.116])

$$\boxed{\Omega P = \bar{\Omega}P + \sum_{n=1}^{\infty} \frac{\delta^n\bar{\Omega}}{\delta\mathcal{E}^n} \, \left(V_{\text{eff}}\right)^n} \tag{61}$$

which we shall now verify.

In order to prove the relation above, we start by using this relation to form the difference ratio

$$\begin{aligned}
\frac{\delta\Omega}{\delta\mathcal{E}} &= \frac{\delta\bar{\Omega}}{\delta\mathcal{E}} + \frac{\delta^2\bar{\Omega}}{\delta\mathcal{E}^2}\, V_{\text{eff}} + \frac{\delta^3\bar{\Omega}}{\delta\mathcal{E}^3}\, (V_{\text{eff}})^2 + \cdots + \frac{\delta\bar{\Omega}}{\delta\mathcal{E}}\frac{\delta V_{\text{eff}}}{\delta\mathcal{E}} + \frac{\delta^2\bar{\Omega}}{\delta\mathcal{E}^2}\, V_{\text{eff}}\frac{\delta V_{\text{eff}}}{\delta\mathcal{E}} + \cdots \\
&= \sum_{n=1}^{\infty} \frac{\delta^n\bar{\Omega}}{\delta\mathcal{E}^n}\, (V_{\text{eff}})^{(n-1)}\left[1 + \frac{\delta V_{\text{eff}}}{\delta\mathcal{E}}\right].
\end{aligned} \tag{62}$$

(It should be noted that the different V_{eff} operators are in general associated with different energies, as explained in Appendix B, Eq. B8.) Next, we take the time derivative of the relation (53), using the relation (43), which yields

$$V_{\text{eff}} = \left[1 + \frac{\delta V_{\text{eff}}}{\delta\mathcal{E}}\right]\bar{V}_{\text{eff}}. \tag{63}$$

This gives with the relation (62)

$$\frac{\delta\Omega}{\delta\mathcal{E}}\,\bar{V}_{\text{eff}} = \sum_{n=1}^{\infty}\frac{\delta^n\bar{\Omega}}{\delta\mathcal{E}^n}\,(V_{\text{eff}})^n, \tag{64}$$

and with the relation (53) we retrieve the relation (61), which is then proven.

In order to obtain more Bloch-like relations, we first introduce the *reaction operator*, which is the effective interaction (43), apart from the projection operators,

$$V_{\text{R}} = \left[\mathrm{i}\frac{\partial}{\partial t}\widetilde{U}(t)\right]_{t=0}. \tag{65}$$

This gives $V_{\text{eff}} = PV_{\text{R}}P$, and the reaction operator is equal to the wave operator, apart from the resolvent,

$$Q\widetilde{U}(0) = Q\Omega = \Gamma_Q V_{\text{R}}. \tag{66}$$

We also introduce the operator

$$\bar{V}_{\text{R}} = \left[\mathrm{i}\frac{\partial}{\partial t}\bar{U}(t)\right]_{t=0}, \tag{67}$$

where $\bar{U}$ is the evolution operator without MSC. This leads in analogy with the relation (66) to

$$Q\bar{U}(0) = Q\bar{\Omega} = \Gamma_Q\bar{V}_{\text{R}}. \tag{68}$$

Using the rule for differentiating a product, developed in Appendix B (Eq. B4), and the relation

$$\frac{\delta^m\Gamma_Q}{\delta\mathcal{E}^m} = -\Gamma_Q\frac{\delta^{(m-1)}\Gamma_Q}{\delta\mathcal{E}^{(m-1)}}, \tag{69}$$

we can express the difference ratios of $\bar{\Omega}$ as

$$\frac{\delta^n\bar{\Omega}}{\delta\mathcal{E}^n} = \frac{\delta^n(\Gamma_Q\bar{V}_{\text{R}})}{\delta\mathcal{E}^n} = \sum_{m=0}^{n}\frac{\delta^m\Gamma_Q}{\delta\mathcal{E}^m}\frac{\delta^{(n-m)}\bar{V}_{\text{R}}}{\delta\mathcal{E}^{(n-m)}} = \Gamma_Q\frac{\delta^n\bar{V}_{\text{R}}}{\delta\mathcal{E}^n} - \sum_{m=1}^{n}\Gamma_Q\frac{\delta^{(m-1)}\Gamma_Q}{\delta\mathcal{E}^{(m-1)}}\frac{\delta^{(n-m)}\bar{V}_{\text{R}}}{\delta\mathcal{E}^{(n-m)}}. \tag{70}$$

The last term can be expressed

$$-\Gamma_Q\sum_{m=0}^{n-1}\frac{\delta^m\Gamma_Q}{\delta\mathcal{E}^m}\frac{\delta^{(n-m)}\bar{V}_{\text{R}}}{\delta\mathcal{E}^{(n-m)}} = -\Gamma_Q\frac{\delta^{(n-1)}\bar{\Omega}}{\delta\mathcal{E}^{(n-1)}}. \tag{71}$$

Inserted in the expansion (61), this yields

$$\boxed{Q\Omega P = Q\bar{\Omega}P - \Gamma_Q\Omega V_{\text{eff}} + \Gamma_Q\sum_{n=1}^{\infty}\frac{\delta^n\bar{V}_{\text{R}}}{\delta\mathcal{E}^n}\,(V_{\text{eff}})^n} \tag{72}$$

This equation will later be used to derive the Bloch equations for energy-dependent interactions.
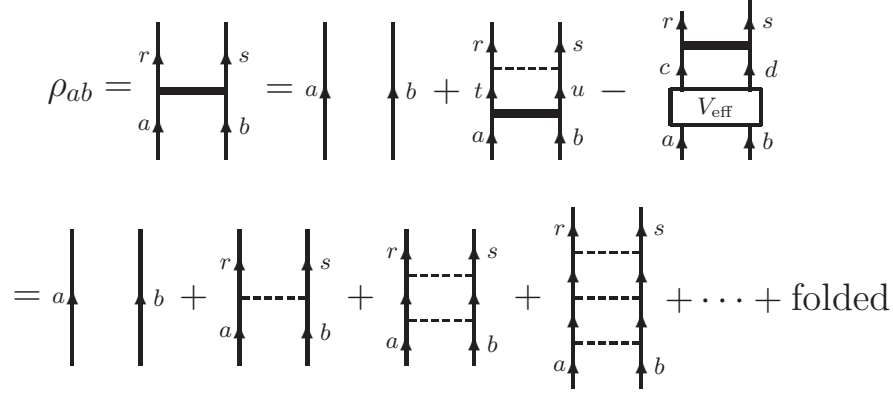
FIG. 3: Graphic representation of pair functions ρ_{ab} generated by the pair equation (75).

B. Instantaneous interactions

The instantaneous Coulomb interaction can be treated essentially as in standard (relativistic) many-body theory, and we start by recalling the treatment of the correlation effect for a two-electron system. The wave operator in the coupled-cluster formalism (10) can then be expressed [1]

$$\Omega = 1 + S_2, \tag{73}$$

where S_2 is the two-body cluster operator. Operating on a model-space state, yields a *pair function*

$$|\rho_{ab}\rangle = \Omega|ab\rangle = |ab\rangle + s_{ab}^{rs}|rs\rangle. \tag{74}$$

Inserting the pair function into the Bloch equation (11), yields the corresponding pair equation

$$\big(\varepsilon_a + \varepsilon_b - h_0(1) - h_0(2)\big)|\rho_{ab}\rangle = |rs\rangle\langle rs|V_{12}|\rho_{ab}\rangle - |\rho_{cd}\rangle\langle cd|V_{\text{eff}}|ab\rangle. \tag{75}$$

The last term is the *folded* term and is the result of the reduction of singularities which appear when the intermediate states lie in the model space, which we have referred to above as *model-space contribution* (MSC). When the equation is solved iteratively, the Coulomb interactions are generated to all orders, as illustrated in Fig. 3. This is the type of pair functions we have been using in our many-body calculations for several decades [27, 28, 29, 30, 31].

We denote the wave operator with only Coulomb interactions by Ω_{I} and the part with no folded diagrams by $\bar{\Omega}_{\text{I}}$. Then we have

$$\bar{\Omega}_{\text{I}}P = \Big[1 + \Gamma_Q V_{12} + \Gamma_Q V_{12}\Gamma_Q V_{12} + \cdots\Big]P, \tag{76}$$

and using the relations (72) and (61), this leads to the standard Bloch equation (8)

$$\boxed{\big[\Omega_{\text{I}}, H_0\big]P = V_{12}\Omega_{\text{I}}P - \Omega_{\text{I}}\,V_{\text{eff}}} \tag{77}$$

C. Combined instantaneous and retarded interactions

We shall now find Bloch equations for the *combined* retarded and instantaneous interactions. In the Coulomb gauge the function $f(\boldsymbol{x}_1, \boldsymbol{x}_2, k)$, involved in the exchange of a retarded photon, is given by the expression (47), which can be separated into products of single-electron operators, as shown in Appendix A,

$$f_{\text{C}}(\boldsymbol{x}_1, \boldsymbol{x}_2, k) = \frac{e^2 k}{4\pi^2}\sum_{l=0}^{\infty}\Big[-(2l+1)V_{\text{G}}^l(kr_1)\cdot V_{\text{G}}^l(kr_2) + \frac{1}{2l+1}V_{\text{SR}}^l(kr_1)\cdot V_{\text{SR}}^l(kr_2)\Big]. \tag{78}$$

The two terms represent the Gaunt and scalar-retardation parts, respectively, and we shall treat each of them as the result of *two* perturbations, namely $V_{\text{G}}^l(kr_1)$ and $V_{\text{G}}^l(kr_2)$ in the case of the Gaunt interaction and $V_{\text{SR}}^l(kr_1)$ and

$V_{\text{SR}}^l(kr_2)$ for the scalar retardation—of course, with the appropriate factors and with summation over the angular momentum of the photon, l, and integration over space and the linear photon momentum, k.

The photon can also be absorbed by the same electron, leading to self-energy and vertex-correction contributions, as we shall briefly indicate below.

The perturbations above are time-independent in the Schrödinger picture, and we can then apply the Gell-Mann–Low theorem (22), which leads to the Schrödinger-like equation (24)

$$\left(\boldsymbol{H}_0 + H'\right)\boldsymbol{\Psi}^\alpha = E^\alpha \boldsymbol{\Psi}^\alpha, \tag{79}$$

where H' is given by the instantaneous Coulomb interaction $V_{\text{I}} = V_{12}$ and the two retarded components $V_{\text{G}}^l(kr)$ and $V_{\text{SR}}^l(kr)$. The wave function lies here in an *extended Fock space* with variable number of uncontracted, virtual photons, which we indicate by using the bold-face symbol $\boldsymbol{\Psi}^\alpha$. The bold-face symbol $\boldsymbol{H}_0$ represents the model Hamiltonian including the radiation field (27). We also introduce a *Fock-space wave operator* in analogy with the standard wave operator (5)

$$\boldsymbol{\Psi}^\alpha = \boldsymbol{\Omega}\boldsymbol{\Psi}_0^\alpha. \tag{80}$$

The resolvent (40) is now generalized to

$$\boldsymbol{\Gamma}_{\boldsymbol{Q}}(\mathcal{E}) = \frac{\boldsymbol{Q}}{\mathcal{E} - \boldsymbol{H}_0} \tag{81}$$

when operating on a model-space state of energy $\mathcal{E}$. $\boldsymbol{Q} = 1 - P$ is here the projection operator for the complementary Fock space, for a two-electron system given by

$$\boldsymbol{Q} = |rs\rangle\langle rs| + |ij, k\rangle\langle ij, k| + \cdots \tag{82}$$

The first term represents the part of the operator in the restricted space with no photons (c.f. Eq. 36) with $|rs\rangle$ being a state outside the model space. The second term represents the part with one photon, with $|ij\rangle$ being an arbitrary state, etc.
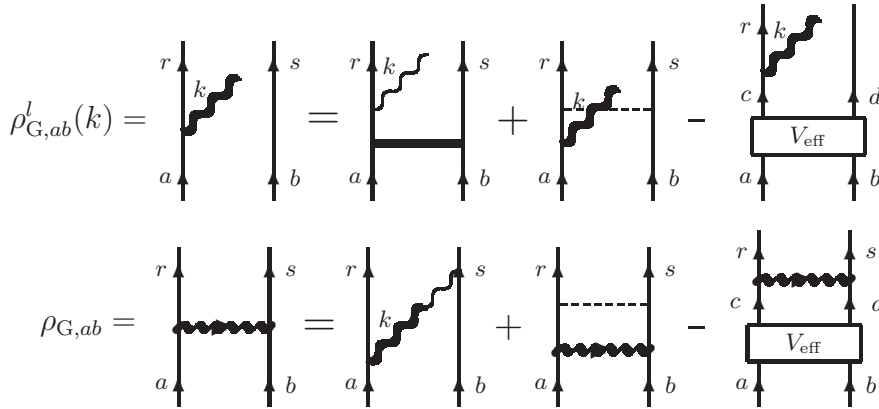

FIG. 4: Graphical representation the pair equations (91), solving the Bloch equation equations (88) and (90).

In order to treat the case where the instantaneous interactions cross a retarded photon, we have to apply the former *between* the two perturbations of the retarded interaction. We denote the wave operator with an "uncontracted" retarded photon and an arbitrary number of instantaneous interactions before and after the retarded photon is created by $\Omega_{\text{G}}^l(k)$ and $\Omega_{\text{SR}}^l(k)$, respectively, for the two components of the retarded interaction. The components of these operators with no model-space contributions are in analogy with previous cases denoted by $\bar{\Omega}_{\text{G}}^l(k)$ and $\bar{\Omega}_{\text{SR}}^l(k)$, respectively. We then have for the Gaunt interaction (and similarly in the scalar-retardation case)

$$\bar{\Omega}_{\text{G}}^l(k)P = \left(1 + \boldsymbol{\Gamma}_{\boldsymbol{Q}}V_{12} + \boldsymbol{\Gamma}_{\boldsymbol{Q}}V_{12}\boldsymbol{\Gamma}_{\boldsymbol{Q}}V_{12} + \cdots\right)\boldsymbol{\Gamma}_{\boldsymbol{Q}}V_{\text{G}}^l(k)\left(1 + \Gamma_Q V_{12} + \Gamma_Q V_{12}\Gamma_Q V_{12} + \cdots\right)P. \tag{83}$$

The rightmost bracket represents the wave operator $\bar{\Omega}_{\text{I}}$ (76), which leads to

$$\bar{\Omega}_{\text{G}}^l(k)P = \boldsymbol{\Gamma}_{\boldsymbol{Q}}V_{\text{G}}^l(k)\bar{\Omega}_{\text{I}}P + \boldsymbol{\Gamma}_{\boldsymbol{Q}}V_{12}\bar{\Omega}_{\text{G}}^l(k)P. \tag{84}$$
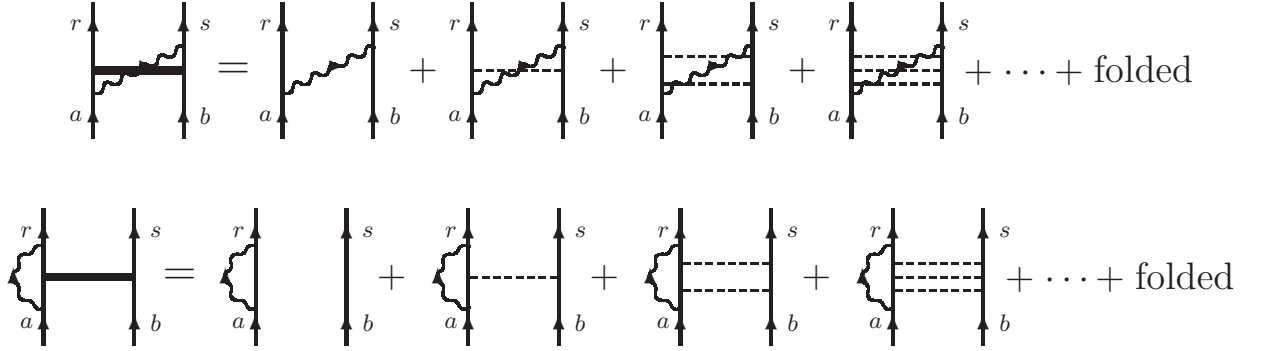
FIG. 5: Graphical representation of a single retarded photon with crossing Coulomb interactions and without Coulomb interactions before and after the retarded interaction.

Inserting this into the expression (72), yields

$$Q\Omega_{\mathrm{G}}^l(k)P = \boldsymbol{\Gamma_Q} \sum_{n=0}^{\infty} \frac{\delta^n(V_{\mathrm{G}}^l(k)\bar{\Omega}_{\mathrm{I}})}{\delta\mathcal{E}^n} (V_{\mathrm{eff}})^n + \boldsymbol{\Gamma_Q} \sum_{n=0}^{\infty} \frac{\delta^n(V_{12}\bar{\Omega}_{\mathrm{G}}^l(k))}{\delta\mathcal{E}^n} (V_{\mathrm{eff}})^n - \boldsymbol{\Gamma_Q}\Omega_{\mathrm{G}}^l(k)V_{\mathrm{eff}}, \tag{85}$$

Since V_{12} as well as $V_{\mathrm{G}}^l(k)$ are energy independent, we have

$$\sum_{n=0}^{\infty} \frac{\delta^n(V_{\mathrm{G}}^l(k)\bar{\Omega}_{\mathrm{I}})}{\delta\mathcal{E}^n} (V_{\mathrm{eff}})^n = V_{\mathrm{G}}^l(k) \sum_{n=0}^{\infty} \frac{\delta^n\bar{\Omega}_{\mathrm{I}}}{\delta\mathcal{E}^n} (V_{\mathrm{eff}})^n = V_{\mathrm{G}}^l(k)\,\Omega_{\mathrm{I}}P \tag{86}$$

again using the expansion (61) and the rule (B4). Treating the second sum similarly, leads to

$$Q\Omega_{\mathrm{G}}^l(k)P = \boldsymbol{\Gamma_Q}V_{\mathrm{G}}^l(k)\,\Omega_{\mathrm{I}}P + \boldsymbol{\Gamma_Q}V_{12}\Omega_{\mathrm{G}}^l(k)P - \boldsymbol{\Gamma_Q}\Omega_{\mathrm{G}}^l(k)V_{\mathrm{eff}} \tag{87}$$

and to the Bloch equation

$$\boxed{\left[\Omega_{\mathrm{G}}^l(k), \boldsymbol{H}_0\right]P = V_{\mathrm{G}}^l(k)\Omega_{\mathrm{I}}P + V_{12}\Omega_{\mathrm{G}}^l(k)P - \Omega_{\mathrm{G}}^l(k)V_{\mathrm{eff}}} \tag{88}$$

In the next step the photon of the function $\Omega_{\mathrm{G}}^l(k)$ is being absorbed by the other electron, followed by additional Coulomb iterations. We denote the corresponding wave operator by Ω_G. Omitting for the time being the MSC associated with the Coulomb interactions, this leads to

$$\bar{\Omega}_G P = \left(1 + \Gamma_Q V_{12} + \Gamma_Q V_{12}\Gamma_Q V_{12} + \cdots\right) \Gamma_Q V_{\mathrm{G}}^l(k)\,\Omega_{\mathrm{G}}^l(k)P, \tag{89}$$

integrating over k and summing over l according to the relation (78). The MSC are as before obtained by inserting this relation into the formula (72), which—using the same argument as before—yields

$$\boxed{\left[\Omega_{\mathrm{G}}, H_0\right]P = V_{\mathrm{G}}^l(k)\,\Omega_{\mathrm{G}}^l(k)P + V_{12}\Omega_{\mathrm{G}}P - \Omega_{\mathrm{G}}V_{\mathrm{eff}}} \tag{90}$$

The framed equations above represent our main equations for dealing with the combined retarded and unretarded interactions. For a two-electron system they can be converted to the pair equations

$$\begin{aligned}
\left(\varepsilon_a + \varepsilon_b - h_0(1) - h_0(2) - k\right)|\rho_{\mathrm{G},ab}^l(k)\rangle &= |rs\rangle\langle rs|V_{\mathrm{G}}^l(k)|\rho_{ab}\rangle + |rs\rangle\langle rs|V_{12}|\rho_{\mathrm{G},ab}^l(k)\rangle - |\rho_{\mathrm{G},cd}^l(k)\rangle\langle cd|V_{\mathrm{eff}}|ab\rangle \\
\left(\varepsilon_a + \varepsilon_b - h_0(1) - h_0(2)\right)|\rho_{\mathrm{G},ab}\rangle &= |rs\rangle\langle rs|V_{\mathrm{G}}^l(k)|\rho_{\mathrm{G},ab}^l(k)\rangle + |rs\rangle\langle rs|V_{12}|\rho_{\mathrm{G},ab}\rangle - |\rho_{cd}\rangle\langle cd|V_{\mathrm{eff}}|ab\rangle.
\end{aligned} \tag{91}$$

Note that the first of these equations is deduced from the relation (88) with the extended $\boldsymbol{H}_0$, which leads to the momentum k on the left-hand side. These equations, which can be solved using standard technique [32, 33], are illustrated in Fig. 4. In Figs 5 and 6 (upper line) we show more explicitly the diagrams involved in the process just described—in the former case without any Coulomb interactions before and after the retarded interaction and in the latter case with such interactions. When the photon is instead absorbed by the same electron as it is emitted from, we get the corresponding self-energy and vertex-correction effects—of course, after appropriate renormalization— as indicated in the bottom lines of the same figures.
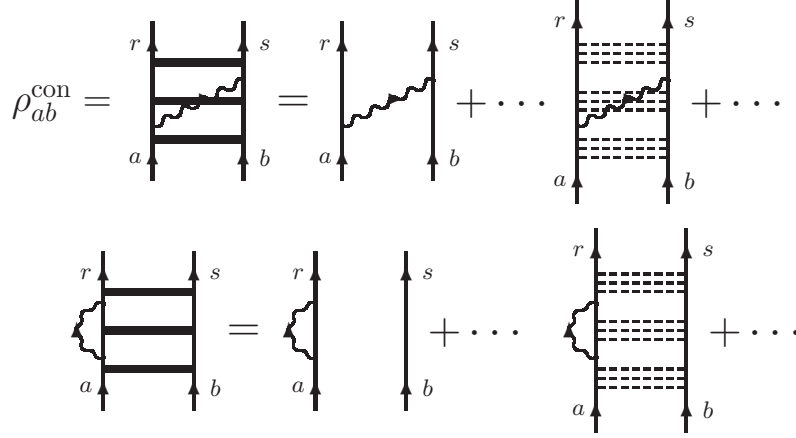
FIG. 6: Graphical representation of a single retarded photon with crossing Coulomb interactions and with Coulomb interactions before and after the retarded interaction. The diagrams in upper line are obtained by solving the pair equations (91) and those in lower line by analogous equation.
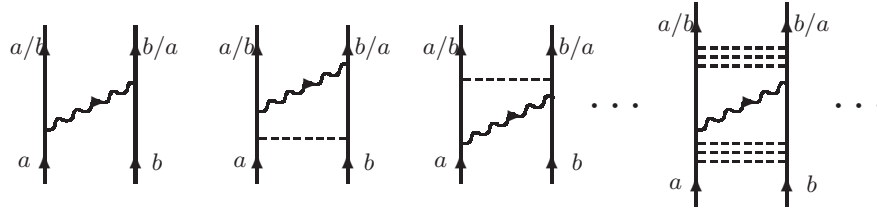

FIG. 7: Diagrams evaluated for the $1s2s\,^1S$ and $1s2s\,^3S$ states of heliumlike neon with the results given in Table I.

D. Derivation of the general Bloch equations

The Bloch equations derived above are valid only in the case of no more than one uncontracted photon at each instance. In order to derive the more general *Fock-space Bloch equation*, we can proceed exactly as in the energy-independent case [21], starting from the Schrödinger-like equation (79). We first project this equation on the model space

$$P\big(\boldsymbol{H}_0 + H'\big)\boldsymbol{\Omega}\boldsymbol{\Psi}_0^\alpha = \boldsymbol{H}_0\boldsymbol{\Psi}_0^\alpha + PH'\boldsymbol{\Omega}\boldsymbol{\Psi}_0^\alpha = E^\alpha\boldsymbol{\Psi}_0^\alpha, \tag{92}$$

using the fact that P and $\boldsymbol{H}_0$ commute, and then operate from the left with $\boldsymbol{\Omega}$

$$\boldsymbol{\Omega}\boldsymbol{H}_0\boldsymbol{\Psi}_0^\alpha + \boldsymbol{\Omega}PH'\boldsymbol{\Omega}\boldsymbol{\Psi}_0^\alpha = E^\alpha\boldsymbol{\Psi}^\alpha. \tag{93}$$

Subtracting the original SE (24), then yields the *Fock-space Bloch equation*

$$\boxed{\big[\boldsymbol{\Omega}, \boldsymbol{H}_0\big]P = H'\boldsymbol{\Omega}P - \boldsymbol{\Omega}V_{\text{eff}}\,; \qquad \boldsymbol{H}_{\text{eff}} = P\boldsymbol{H}_0P + V_{\text{eff}}\,; \qquad V_{\text{eff}} = PH'\boldsymbol{\Omega}P} \tag{94}$$

The solution can be expressed

$$\boxed{\boldsymbol{Q}\boldsymbol{\Omega}P = \boldsymbol{\Gamma}_{\boldsymbol{Q}}\big(H'\boldsymbol{\Omega} - \boldsymbol{\Omega}V_{\text{eff}}\big)P} \tag{95}$$

where $\boldsymbol{\Gamma}_{\boldsymbol{Q}}$ is the generalized resolvent (81).

We can expand the Fock-space wave operator and resolvent into components acting in the subspace with no photons, with one photon etc. as

$$\begin{cases} \boldsymbol{\Omega} = \Omega + \Omega^+ + \cdots \\ \boldsymbol{\Gamma}_{\boldsymbol{Q}} = \Gamma_Q + \Gamma_Q^+ \cdots \end{cases} \tag{96}$$
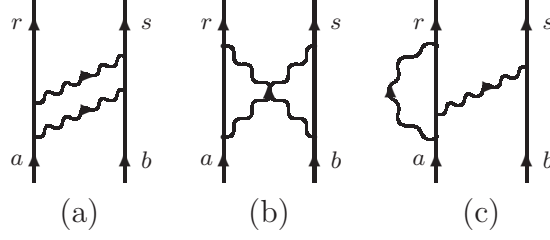
FIG. 8: Some irreducible diagrams, not included in the procedure described here.
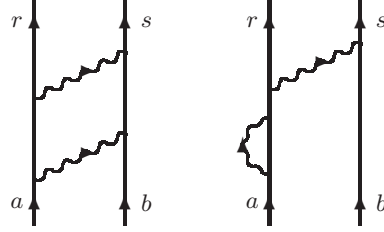

FIG. 9: Examples of reducible diagrams, obtained by repeated use of the procedure described.

The generalized Bloch equation (95) can then be separated into

$$
\begin{cases}
\Omega P = P + \Gamma_Q \Big[V_{12}\Omega + \overline{V_{\text{Ret}}\Omega^+} - \Omega V_{\text{eff}} \Big] P \\
\Omega^+ P = \Gamma_Q^+ \Big[V_{\text{Ret}}\Omega + V_{12}\Omega^+ + \overline{V_{\text{Ret}}\Omega^{++}} - \Omega^+ V_{\text{eff}} \Big] P \\
\Omega^{++} P = \cdots
\end{cases}
\tag{97}
$$

The hook represents integration over the photon momentum k and summation over the angular momentum l, according to the single-photon expression (78). These equations are valid also in the case of multiple free photons at the same time. Considering at most a single free photon, we see that they lead to the Bloch equations (88) and (90) derived above.

V.   NUMERICAL PROCEDURE AND RESULTS

The pair equations considered here can be solved numerically with essentially the same technique as developed by Salomonson and Öster for (relativistic) many-body calculations [32, 33] and used in our previous works [3, 34]. The radial integrations are performed with an exponential grid with 70-150 grid points and the k integration with 100-150 points using Gaussian quadrature. For excited states poles appear in the k integration, which require special attention (for details, see ref. [34]). The numerical calculations are quite time consuming in the present case, since separate pair functions have to be evaluated for each value of the photon momentum. On the other hand, the procedure is particularly well suite for parallel computing, and we hope that the procedure can be speeded up considerably, when our routines are better optimized.

TABLE I: Effects of one- and two-photon exchange for the excited $1s2s\,^1S$ and ^3S states of heliumlike neon (in μH).

		$1s2s\,^1S$	$1s2s\,^3S$
One-photon	Gaunt	2465.44	171,50
	Scalar ret.	171,58	-171,58
Two-photon	Coul.-Gaunt	-794.8	-51.8
	Coul.-Scal.ret.	22.5	42.5
One + two-photon	Gaunt	1670.7	119.7
	Scal.ret.	194.2	-129.1
One photon correlated	Gaunt	1752.0	124.6
	Scal.ret.	183.9	-132.2

Here, we shall only give some illustrative examples of our numerical results—more results will be published separately [18]. In Table I we show the effect of one retarded photon with one and infinitely many non-crossing Coulomb interactions for the $1s2s\,^1S$ and ^3S states of heliumlike neon. This corresponds to the diagrams shown in Fig. 7, excluding virtual pairs (NVP). This represents the first numerical evaluation of effects beyond two-photon exchange, involving a retarded interaction. The two-photon effects have been compared with the corresponding S-matrix results [34] and are found to agree to 3-4 digits, which represents the numerical accuracy of the present calculations. The effect of correlation beyond second order is in this case found to be about five percent of the total contribution, which is one order of magnitude larger than the effect of the retarded (reducible and irreducible) two-photon interaction [34]. The effect of virtual pairs is of the same order as that of two retarded interactions. This indicates that for heliumlike neon the procedure described here with a single retarded photon together with Coulomb interactions represents about 99 % of the non-radiative effects not included in a standard many-body perturbation treatment with only instantaneous Coulomb interactions. For lighter elements the importance of a single retarded photon is even more pronounced.

VI. SUMMARY AND OUTLOOK

We have in previous articles described a new technique for QED calculations that we refer to as the covariant evolution-operator (CEO) method [2, 3, 4, 5]. This method has the great advantage compared to other QED techniques that it has a structure very akin to that of standard many-body perturbation theory, which opens up the possibility for a merger of the two techniques. In two previous papers [4, 5] we have indicated how such a merger can be accomplished, and this is developed further in the present paper, and some numerical results are presented. Combined QED and correlation effects, which can be treated only in a very limited fashion by standard techniques, are of particular importance for light and medium-heavy elements. The CEO method also has the advantage compared to the standard S-matrix technique that it can be applied to the case of quasidegeneracy (a property it shares with the two-times Green's-function technique of Shabaev *et al.* [8]).

The procedure we have developed represents the exchange of a single retarded photon and an arbitrary number of instantaneous Coulomb interactions between the electrons, crossing and non-crossing. So far we have been working with positive-energy intermediate states—no-virtual-pair (NVP) approximation—but single and double virtual pairs can be included in the procedure. The procedure can also be used—with proper renormalizations—for radiative effects (self energy and vertex corrections) with a single retarded photon (see Figs 6 and 5). In principle, the procedure can be used also for *irreducible* multi-photon effects, where retarded interactions overlap in time, like those indicated in Fig. 8, by treating more than one uncontracted photon at a particular time. At present, however, this is beyond reach with the computers we have available. On the other hand, *reducible* multi-photon effects, where the interactions are separated in time, as illustrated in Fig. 9, can be included by repeated use of the procedure described.

It has been demonstrated that one retarded photon with Coulomb interaction represents by far the dominating part of the non-radiative multi-photon exchange for light and medium-heavy elements beyond the standard Coulomb correlation (of the order of 99 % for heliumlike neon), and the situation can be expected to be similar for the radiative part. The small effects due to two irreducible retarded photons without Coulomb interactions can be evaluated with standard QED methods, and higher-order effects can with good accuracy be estimated by means of analytical approximations. Therefore, it is our belief that the method presented here, when the routines are fully developed, should be able to produce accurate results for energy separations, such as the fine-structure separations, for light and medium-heavy elements, hopefully down to neutral helium.

APPENDIX A: COULOMB-GAUGE INTERACTION

The terms in the Coulomb-gauge expression (47) can be separated into a product of two single-particle potentials by the spherical wave expansion, using the relation

$$\frac{\sin(kr_{12})}{r_{12}} = k\sum_{l=0}^{\infty}(2l+1)j_l(kr_1)j_l(kr_2)\boldsymbol{C}^l(1)\cdot\boldsymbol{C}^l(2), \tag{A1}$$

where $\boldsymbol{C}^l$ is a spherical tensor, associated with the spherical harmonics Y^l. The Gaunt term then becomes

$$-k\sum_{l=0}^{\infty}(2l+1)V_{\mathrm{G}}^l(kr_1)\cdot V_{\mathrm{G}}^l(kr_2), \tag{A2}$$

where $V_{\mathrm{G}}^l(kr_i)$ is

$$V_{\mathrm{G}}^l(kr) = \boldsymbol{\alpha}\,j_l(kr)\boldsymbol{C}^l. \tag{A3}$$

For the scalar-retardation term we use the relation [35, Sect. 5.7], [36, Part II, App. A]

$$\nabla[f(r)C_m^l] = \frac{1}{2l+1}\Big[-\sqrt{(l+1)(2l+3)}(\frac{d}{dr}-\frac{l}{r})f(r)\boldsymbol{C}_m^{l,l+1}$$
$$+\sqrt{l(2l-1)}(\frac{d}{dr}+\frac{l+1}{r})f(r)\boldsymbol{C}_m^{l,l-1}\Big], \tag{A4}$$

where $\boldsymbol{C}_m^{l,l\pm1}$ is a vector, associated with the vector spherical harmonics $\boldsymbol{Y}_m^{l,l\pm1}$, and the relation

$$\boldsymbol{\alpha}\cdot\boldsymbol{C}_m^{l,k} = \big\{\boldsymbol{\alpha}\,\boldsymbol{C}^l\big\}_m^k, \tag{A5}$$

where the left-hand side is a scalar product and the right-hand side a tensor product. Together with [37]

$$(\frac{d}{dr}-\frac{l}{r})j_l(kr) = -kj_{l+1}(kr) \tag{A6}$$

$$(\frac{d}{dr}+\frac{l+1}{r})j_l(kr) = kj_{l-1}(kr) \tag{A7}$$

the final result of the scalar retardation term becomes

$$\sum_{l=0}^{\infty}\frac{k}{2l+1}V_{\mathrm{SR}}^l(kr_1)\cdot V_{\mathrm{SR}}^l(kr_2), \tag{A8}$$

where expression for the single-particle potentials for the scalar retardation is written as

$$V_{\mathrm{SR}}^l(kr) = \Big[\sqrt{(l+1)(2l+3)}j_{l+1}(kr)\big\{\boldsymbol{\alpha}\,\boldsymbol{C}^{l+1}\big\}^l$$
$$+\sqrt{l(2l-1)}j_{l-1}(kr)\big\{\boldsymbol{\alpha}\,\boldsymbol{C}^{l-1}\big\}^l\Big]. \tag{A9}$$

The function, $f(k)$, in the Coulomb gauge expression (47) then becomes

$$f(k) = \frac{e^2k}{4\pi^2}\sum_{l=0}^{\infty}\Big[-(2l+1)V_{\mathrm{G}}^l(kr_1)\cdot V_{\mathrm{G}}^l(kr_2)+\frac{1}{2l+1}V_{\mathrm{SR}}^l(kr_1)\cdot V_{\mathrm{SR}}^l(kr_2)\Big]. \tag{A10}$$

APPENDIX B: RULES FOR DIFFERENTIATION

The difference ratios we use in the formalism presented here are of a special kind and give rise to special handling rules (see also ref. [5], App. E).

If $A(\mathcal{E})$ is an operator function of the (energy) parameter $\mathcal{E}$, then we define the first-order difference ratio

$$\frac{\delta A(\mathcal{E})}{\delta\mathcal{E}} = \frac{\delta_{\mathcal{E}\mathcal{E}'}A(\mathcal{E})}{\delta\mathcal{E}} = \frac{A(\mathcal{E})-A(\mathcal{E}')}{\mathcal{E}-\mathcal{E}'},$$

Then

$$\frac{\delta}{\delta\mathcal{E}}[A(\mathcal{E})B(\mathcal{E})] = \frac{\delta_{\mathcal{E}\mathcal{E}'}A(\mathcal{E})}{\delta\mathcal{E}}B(\mathcal{E}') + A(\mathcal{E})\frac{\delta_{\mathcal{E}\mathcal{E}'}B(\mathcal{E})}{\delta\mathcal{E}}. \tag{B1}$$

The second difference ratio is defined as

$$\frac{\delta^2 A(\mathcal{E})}{\delta\mathcal{E}^2} = \frac{\delta^2_{\mathcal{E}\mathcal{E}'\mathcal{E}''}A(\mathcal{E})}{\delta\mathcal{E}^2} = \frac{\delta_{\mathcal{E}\mathcal{E}'}}{\delta\mathcal{E}}\frac{\delta_{\mathcal{E}\mathcal{E}''}A(\mathcal{E})}{\delta\mathcal{E}}$$

and generally

$$\frac{\delta^n_{\mathcal{E}\mathcal{E}'\ldots\mathcal{E}^n}}{\delta\mathcal{E}^n} = \frac{\delta_{\mathcal{E}\mathcal{E}'}}{\delta\mathcal{E}}\frac{\delta_{\mathcal{E}\mathcal{E}''}}{\delta\mathcal{E}}\cdots\frac{\delta_{\mathcal{E}\mathcal{E}^n}}{\delta\mathcal{E}}.$$

It then follows that

$$\frac{\delta^2}{\delta\mathcal{E}^2}[A(\mathcal{E})B(\mathcal{E})] = \frac{\delta^2_{\mathcal{E}\mathcal{E}'\mathcal{E}''}}{\delta\mathcal{E}^2}[A(\mathcal{E})B(\mathcal{E})] = \frac{\delta_{\mathcal{E}\mathcal{E}'}}{\delta\mathcal{E}}\frac{\delta_{\mathcal{E}\mathcal{E}''}}{\delta\mathcal{E}}[A(\mathcal{E})B(\mathcal{E})]$$

$$= \frac{\delta_{\mathcal{E}\mathcal{E}'}}{\delta\mathcal{E}}\left[\frac{\delta_{\mathcal{E}\mathcal{E}''}A(\mathcal{E})}{\delta\mathcal{E}}B(\mathcal{E}'') + A(\mathcal{E})\frac{\delta_{\mathcal{E}\mathcal{E}''}B(\mathcal{E})}{\delta\mathcal{E}}\right]$$

$$= \frac{\delta^2 A_{\mathcal{E}\mathcal{E}'\mathcal{E}''}(\mathcal{E})}{\delta\mathcal{E}^2}B(\mathcal{E}'') + \frac{\delta_{\mathcal{E}\mathcal{E}'}A(\mathcal{E})}{\delta\mathcal{E}}\frac{\delta_{\mathcal{E}\mathcal{E}''}B(\mathcal{E})}{\delta\mathcal{E}} + A(\mathcal{E})\frac{\delta^2_{\mathcal{E}\mathcal{E}'\mathcal{E}''}B(\mathcal{E})}{\delta\mathcal{E}^2}. \tag{B2}$$

It should be noted that the operator $B(\mathcal{E}'')$ is unaffected by the differentiation $\delta_{\mathcal{E}\mathcal{E}'}$. With simplified notations we then have

$$\frac{\delta^2(AB)}{\delta\mathcal{E}^2} = \frac{\delta^2 A}{\delta\mathcal{E}^2}B + \frac{\delta A}{\delta\mathcal{E}}\frac{\delta B}{\delta\mathcal{E}} + A\frac{\delta^2 B}{\delta\mathcal{E}^2}, \tag{B3}$$

which can be generalized to

$$\boxed{\frac{\delta^n(AB)}{\delta\mathcal{E}^n} = \sum_{m=0}^{n}\frac{\delta^m A}{\delta\mathcal{E}^m}\frac{\delta^{(n-m)}B}{\delta\mathcal{E}^{(n-m)}}} \tag{B4}$$

In the case of complete degeneracy we have in first order

$$\lim_{\mathcal{E}'\to\mathcal{E}}\frac{\delta_{\mathcal{E}\mathcal{E}'}A(\mathcal{E})}{\delta\mathcal{E}} = \frac{\partial A(\mathcal{E})}{\partial\mathcal{E}}, \tag{B5}$$

while in second order we have

$$\lim_{\mathcal{E}',\mathcal{E}''\to\mathcal{E}}\frac{\delta^2_{\mathcal{E}\mathcal{E}'\mathcal{E}''}A(\mathcal{E})}{\delta\mathcal{E}^2} = \frac{1}{2}\frac{\partial^2 A(\mathcal{E})}{\partial\mathcal{E}^2} \tag{B6}$$

and generally

$$\boxed{\lim_{\mathcal{E}',\mathcal{E}''\cdots\to\mathcal{E}}\frac{\delta^n_{\mathcal{E}\mathcal{E}'\mathcal{E}''}A(\mathcal{E})}{\delta\mathcal{E}^n} = \frac{1}{n!}\frac{\partial^n A(\mathcal{E})}{\partial\mathcal{E}^n}} \tag{B7}$$

If we have a product of effective interactions, then they are separated by model-space states, which generally have different energies,

$$\cdots P''V_{\text{eff}}P'V_{\text{eff}}P,$$

where P corresponds to the energy $\mathcal{E}$, P' to $\mathcal{E}'$ etc. This appears in multiple folded terms, and the effective interactions have the corresponding energy parameter,

$$\cdots P''V_{\text{eff}}(\mathcal{E}')P'V_{\text{eff}}(\mathcal{E})P.$$

If we now form the difference ratio of this product

$$\frac{\delta}{\delta\mathcal{E}}\Big[\cdots P''V_{\text{eff}}(\mathcal{E}')P'V_{\text{eff}}(\mathcal{E})P\Big],$$

implying that the parameter $\mathcal{E}$ is changed, only the last factor is affected, and

$$\frac{\delta}{\delta\mathcal{E}}\big[\cdots P''V_{\text{eff}}(\mathcal{E}')P'V_{\text{eff}}(\mathcal{E})P\big] = \cdots P''V_{\text{eff}}(\mathcal{E}')P'\,\frac{\delta V_{\text{eff}}(\mathcal{E})}{\delta\mathcal{E}}P$$

or generally

$$\boxed{\frac{\delta(V_{\text{eff}})^n}{\delta\mathcal{E}} = (V_{\text{eff}})^{(n-1)}\,\frac{\delta V_{\text{eff}}}{\delta\mathcal{E}}} \tag{B8}$$

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